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(54) Title: CAST IRON INOCULANT AND METHOD FOR PRODUCTION OF CAST IRON INOCULANT			
(57) Abstract			
<p>The invention relates to an inoculant for the manufacture of cast iron with lamellar, compacted or spheroidal graphite wherein said inoculant comprises between 40 and 80 % by weight of silicon, between 0.5 and 10 % by weight of calcium and/or strontium and/or barium, less than 4 % by weight of aluminium, 0-10 % by weight of manganese and/or titanium and/or zirconium, between 0.5 and 10 % by weight of oxygen in the form of one or more metal oxides, the balance being iron. The invention further relates to a method for producing an inoculant for the manufacture of cast iron with lamellar, compacted or spheroidal graphite, providing a base alloy comprising 40 to 80 % by weight of silicon, 0.5 to 10 % by weight of calcium and/or strontium and/or barium, less than 4 % by weight of aluminium, 0-10 % by weight of manganese and/or titanium and/or zirconium, the balance being iron, and adding 0.5 to 10 % by weight of oxygen in the form of one or more metal oxides to the base alloy.</p>			

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Title: Cast iron inoculant and method for production of cast iron inoculant.

5 Technical Field:

The present invention relates to a ferrosilicon based inoculant for the manufacture of cast iron with lamellar, compacted or spheroidal graphite and to a method for production of the inoculant.

10 Background Art:

Cast iron is typically produced in a cupola or induction furnaces, and generally has about 2 to 4 percent carbon. The carbon is intimately mixed in with the iron and the form which the carbon takes in the solidified cast iron is very important to the characteristics of the cast iron. If the carbon takes the form of iron carbide, then the 15 cast iron is referred to as white cast iron and has the physical characteristics of being hard and brittle which in certain applications is undesirable. If the carbon takes the form of graphite, the cast iron is soft and machinable and is referred to as gray cast iron.

20 Graphite may occur in cast iron in the lamellar, compacted or spheroidal forms and variations thereof. The spheroidal form produces the highest strength and most ductile form of cast iron.

25 The form that the graphite takes as well as the amount of graphite versus iron carbide can be controlled with certain additives that promote the formation of graphite during the solidification of cast iron. These additives are referred to as inoculants and their addition to the cast iron as inoculation. In casting iron products from cast iron, the foundryman is continually plagued by the formation of iron carbides in thin sections of the cast. The formation of the iron carbide is brought about by the rapid cooling of 30 the thin sections as compared to the slower cooling of the thicker sections of the cast. The formation of iron carbide in a cast iron product is referred to in the trade as "chill". The formation of chill is quantified by measuring "chill depth" and the power of an inoculant to prevent chill and reduce chill depth is a convenient way in which to measure and compare the power of inoculants.

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There is a constant need to find inoculants which reduce chill depth and improve the machinability of gray and ductile cast irons.

Since the exact chemistry and mechanism of inoculation and why inoculants function as they do is not completely understood, a great deal of research goes into providing the industry with a new inoculant.

- 5 It is thought that calcium and certain other elements suppress the formation of iron carbide and promote the formation of graphite. A majority of inoculants contain calcium. The addition of these iron carbide suppressants is usually facilitated by the addition of a ferrosilicon alloy and probably the most widely used ferrosilicon alloys are the high silicon alloy containing 75 to 80 % silicon and the low silicon alloy 10 containing 45 to 50 % silicon.

U.S. patent No. 3,527,597 discovered that good inoculating power is obtained with the addition of between about 0.1 to 10 % strontium to a silicon-bearing inoculant which contains less than about 0.35 % calcium and up to 5 % aluminium.

- 15 It is further known that if barium is used in conjunction with calcium the two act together to give a greater reduction in chill than an equivalent amount of calcium.

- 20 The suppression of carbide formation is associated by the nucleating properties of the inoculant. By nucleating properties it is understood the number of nuclei formed by an inoculant. A high number of nuclei formed improve the inoculation effectiveness and improves the carbide suppression. Further a high nucleation rate may also give better resistance to fading of the inoculating effect during prolonged holding time of the molten iron after inoculation.

- 25 **Disclosure of Invention:**
It has now been found that the addition of oxygen in the form of metal oxide to ferrosilicon based inoculants containing calcium and/or strontium and/or barium substantially increases the nucleation rate of the inoculant.

- 30 According to a first aspect the present invention relates to an inoculant for the manufacture of cast iron with lamellar, compacted or spheroidal graphite wherein said inoculant comprises between 40 and 80 % by weight of silicon, between 0.5 and 10 % by weight of calcium and/or strontium and/or barium, less than 4 % by weight of 35 aluminium, 0 - 10 % by weight of manganese and/or titanium and/or zirconium, between 0.5 and 10 % by weight of oxygen in the form of one or more metal oxides, the balance being iron.

According to a first embodiment, the inoculant is in the form of a solid mixture of a ferrosilicon based alloy and the metal oxide.

5 According to a second embodiment the inoculant is in the form of a ferrosilicon based alloy containing the metal oxide.

The inoculant according to the present invention preferably comprises 0.5 to 5 % by weight of manganese and/or titanium and/or zirconium.

10 According to a preferred embodiment the metal oxide is selected among FeO, Fe₂O₃, Fe₃O₄, SiO₂, MnO, MgO, Al₂O₃, TiO₂ and CaSiO₂.

The oxygen content of the inoculant is preferably between 1 and 6 % by weight.

15 It has surprisingly been found that the inoculant according to the present invention increases the number of nuclei formed when the inoculant is added to cast iron, thus obtaining an improved suppression of iron carbide formation using the same amount of inoculant as with conventional inoculants, or obtaining the same iron carbide suppression using less inoculant than when using conventional inoculants.

20 According to a second aspect the present invention relates to a method for producing an inoculant for the manufacture of cast iron with lamellar, compacted or spheroidal graphite, comprising providing a base alloy comprising 40 to 80 % by weight of silicon, 0.5 to 10 % by weight of calcium and/or strontium and/or barium, 0 - 10 % by weight of manganese and/or titanium and/or zirconium, less than 4 % by weight of aluminium, the balance being iron, and adding 0.5 to 10 % by weight of oxygen in the form of one or more metal oxides to the base alloy.

30 According to one embodiment of the method the metal oxides are mixed with the base alloy by mechanical mixing of solid base alloy particles and solid metal oxide particles. The mechanical mixing can be carried out in any conventional mixing apparatus which gives a substantially homogeneous mixing, such as for example a rotating drum.

35 According to another embodiment of the method the metal oxides are supplied to a melt of the base alloy whereafter the melt is solidified. The metal oxides are preferably added to the stream of molten base alloy when pouring the alloy into casting moulds. Alternatively the metal oxides may be added in the casting moulds before pouring molten base alloy into the moulds.

EXAMPLE 1**Production of inoculant.**

- 5 Four batches of 7000 grams of 75 % ferrosilicon having a particle size between 0.2 and 1mm and containing about 1 % by weight of calcium, 1 % by weight of barium and 1 % by weight of aluminium were mechanically mixed with different amount of powderous iron oxide materials as shown in table 1. The mixing was carried out using
 10 a combined tilting and rotating drum to obtain homogeneous mixtures of the different inoculants. The oxygen content of the four produced inoculants A through D is also shown in table 1.

Table 1

15

Test mixture No.	Oxide		Total oxygen content in the mixture.
	Type	Weight (g)	
A	Fe ₂ O ₃	350	1.4 wt %
B	Fe ₂ O ₃	700	2.7 wt %
C	Fe ₂ O ₃	1400	5.0 wt %
D	Fe ₃ O ₄	613	2.3 wt %

EXAMPLE 2

- 20 The four inoculants A through D produced in example 1 were used for inoculation of a cast iron containing 3.7 % by weight of carbon, 2.4 % by weight of silicon, 0.1 % by weight of manganese 0.025 % by weight of phosphorus, 0.005 % sulphur and 0.050 % by weight of magnesium. For comparison purposes two tests were made using a conventional base inoculant containing 75 % ferrosilicon, 1 % by weight of
 25 calcium, 1 % by weight of barium and 1 % by weight of aluminium. In each test 0.3 % by weight inoculant was added to the cast iron melts. After casting nodule densities in 5 mm sections of the castings were determined. The results are shown in table 2. Heat No. 1 and 2 refer to tests with the conventional inoculant, while heat No. 3 - 6 in table 2 refer to tests with inoculants A through D according to table 1 in example 1.

Table 2

Heat No.	Inoculant	Nodule density (mm ⁻²)
1	(Ca, Ba, Al) - FeSi	381
2	(Ca, Ba, Al) - FeSi	370
3	(Ca, Ba, Al) - FeSi + Fe ₂ O ₃ (A)	477
4	(Ca, Ba, Al) - FeSi + Fe ₂ O ₃ (B)	624
5	(Ca, Ba, Al) - FeSi + Fe ₂ O ₃ (C)	427
6	(Ca, Ba, Al) - FeSi + Fe ₃ O ₄ (D)	449

- 5 As can be seen from table 2 the inoculants according to the present invention give an increased nodule density compared to the conventional inoculant of up to about 70 %.

EXAMPLE 3

- 10 Production of inoculant.

Four samples of 7000 grams of a conventional inoculant based on 75 % ferrosilicon and containing 1 % by weight of calcium, 1 % by weight of barium and 1 % by weight of aluminium were melted in a graphite crucible using an induction furnace.

15 Small amounts of calcium and barium were added to the liquid alloy to adjust for fading of these elements during melting and holding. The different melts were poured into copper chill moulds while adding various types and amounts of iron oxides to the metal stream and/or to the chill moulds prior to casting. Table 3 gives a summary of the inoculants produced giving the type and amount of iron oxide added and the final

20 chemical composition of the inoculant.

Table 3

Heat No.	Oxide Type Added	Oxide Weight Added	Chemical Composition of Inoculant Alloys Produced (in wt %)				
			% Si	% Ca	% Ba	% Al	% O
E	Fe ₂ O ₃	400 g	73.9	0.61	0.84	0.78	1.83
F	Fe ₃ O ₄	400 g	75.6	0.86	0.95	0.88	1.84
G	Fe ₃ O ₄	633 g	70.2	1.05	1.18	0.84	3.60
H	FeO	785 g	68.1	1.15	1.30	0.94	5.70

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The produced inoculants E through H were subsequently crushed and sieved, and the 0.2 - 1.0 mm fraction of each material were used for cast iron inoculation trials as described in example 4.

10 EXAMPLE 4

The four inoculants E through H produced in sample 3 were used for inoculation of a cast iron containing 3.7 % by weight of carbon, 2.4 % by weight of silicon, 0.1 % by weight of manganese, 0.025 % by weight of phosphorus, 0.005 % sulphur and 0.050 % by weight of magnesium. For comparison purposes one test was made using a conventional base inoculant containing 75 % ferrosilicon, 1 % by weight of calcium, 1 % by weight of barium and 1 % by weight of aluminium. In each test 0.3 % by weight inoculant was added to the cast iron melt. After casting nodule densities in 5 mm sections of the casting were determined. The results are shown in table 4. Heat No. 1 refer to the test with the conventional inoculant, while heat No. 2 - 5 in table 4 refer to tests with inoculants E through H according to table 3 in example 3.

Table 4

Heat No.	Inoculant	Nodule density (mm ⁻²)
1	(Ca, Ba, Al) - FeSi	375
2	(Ca, Ba, Al) - FeSi + Fe ₂ O ₃ (E)	552
3	(Ca, Ba, Al) - FeSi + Fe ₃ O ₄ (F)	524
4	(Ca, Ba, Al) - FeSi + Fe ₃ O ₄ (G)	525
5	(Ca, Ba, Al) - FeSi + FeO (H)	454

- 5 As can be seen from table 4, an increase in nodule density of up to about 50 % was obtained by the inoculants according to the present invention compared to the nodule density obtained by the conventional inoculant.

CLAIMS

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1. An inoculant for the manufacture of cast iron with lamellar, compacted or spheroidal graphite wherein said inoculant comprises between 40 and 80 % by weight of silicon, between 0.5 and 10 % by weight of calcium and/or strontium and/or barium, less than 4 % by weight of aluminium, 0 - 10 % by weight of manganese and/or titanium and/or zirconium, between 0.5 and 10 % by weight of oxygen in the form of one or more metal oxides, the balance being iron.

10 2. Inoculant according to claim 1, characterized in that it is in the form of a solid mixture of a ferrosilicon based alloy and the metal oxide.

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3. Inoculant according to claim 1, characterized in that it is in the form of a ferrosilicon based alloy containing the metal oxide.

20 4. Inoculant according to claims 1 - 3, characterized in that the metal oxide is selected among FeO, Fe₂O₃, Fe₃O₄, SiO₂, MnO, MgO, Al₂O₃, TiO₂ and CaSiO₂.

25 5. Inoculant according to claims 1 - 4, characterized in that the oxygen content is between 1 and 6 % by weight.

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6. Inoculant according to claims 1 - 5, characterized in that the inoculant comprises between 0.5 and 5 % by weight of manganese and/or titanium and/or zirconium.

30 7. A method for producing an inoculant for the manufacture of cast iron with lamellar, compacted or spheroidal graphite, providing a base alloy comprising 40 to 80 % by weight of silicon, 0.5 to 10 % by weight of calcium and/or strontium and/or barium, less than 4 % by weight of aluminium, 0 - 10 % by weight of manganese and/or titanium and/or zirconium, the balance being iron, and adding 0.5 to 10 % by weight of oxygen in the form of one or more metal oxides to the base alloy.

35 8. Method according to claim 7, characterized in that the metal oxides are mixed with the base alloy by mechanical mixing of solid base alloy particles and solid metal oxide particles.

9. Method according to claim 7, characterized in that the metal oxides are supplied to a melt of the base alloy whereafter the melt is solidified.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 95/00029

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C21C 1/10, C22C 33/08
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C21C, C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A2, 0232042 (ELKEM METALS COMPANY), 12 August 1987 (12.08.87), page 11, line 25 - line 50, claims 1-16 --	1-9
A	EP, A1, 0524444 (SKW TROSTBERG AKTIENGESELLSCHAFT), 27 January 1993 (27.01.93), claims 1-3 -- -----	1-9

 Further documents are listed in the continuation of Box C. See patent family annex.

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Information on patent family members

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Patent document cited in search report	Publication date		Patent family member(s)	Publication date
EP-A2- 0232042	12/08/87		SE-T3- 0232042 AU-A- 6786587 30/07/87 CA-A- 1300894 19/05/92 DE-A- 3773952 28/11/91 JP-C- 1778127 28/07/93 JP-B- 4056082 07/09/92 JP-A- 62180010 07/08/87 SU-A- 1813113 30/04/93 US-A- 4666516 19/05/87 US-A- 4749549 07/06/88	
EP-A1- 0524444	27/01/93		DE-C- 4124159 09/04/92 US-A- 5209901 11/05/93	